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INTERNAL ENERGY TRANSFER AND DISSOCIATION MODEL DEVELOPMENT USING ACCELERATED FIRST-PRINCIPLES SIMULATIONS OF HYPERSONIC FLOW FEATURES [FINAL REPORT - YOUNG INVESTIGATOR PROGRAM (YIP) 2010]

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DOCUMENT CONTENTS:

Major Contributions Include:

1) **All-atom computational chemistry (molecular dynamics – MD) simulation of normal shock waves is now possible.** Pure MD simulations were validated with experimental data for shock structure. The only model input into such simulations is the potential energy surface (PES) that governs individual atomic interaction forces, developed by chemists and physicists.

2) In contrast to existing rotational energy models, we found that the rotational relaxation rate (τ_{rot}) depends strongly on the initial degree of nonequilibrium and the direction towards the equilibrium state. Compressing flows involve fast excitation whereas expanding flows involve slow relaxation for the same equilibrium temperature. **We developed a new rotation model for both DSMC and CFD simulation.**

3) At high temperatures we found clear evidence of rotational-vibrational energy coupling. Existing models using relaxation times (τ_{rot} and τ_{vib}) are not able to reproduce the ro-vibrational coupling found in MD simulations. **We propose that an additional relaxation time ($\tau_{rot\text{-}vib}$) is required to model direct energy transfer between rotation and vibration at high temperatures and we presented a new ro-vibrational model.** Preliminary simulations for dissociating nitrogen were also demonstrated.

4) **A numerical method that replaces the collision model in DSMC with MD trajectories was developed and shown to reproduce exactly pure MD results.** This enables simulation of axisymmetric and even 3D flows where a potential energy surface is the only model input. Thus, the accuracy of pure MD is maintained for full flow fields; directly linking computational chemistry with aerothermodynamics.

I. Publications

Journal Articles (5):

Valentini, P., Norman, P., Zhang, C., and Schwartzentruber, T.E., "Coupled Rotation Vibration Energy Transfer in High Temperature Nitrogen", submitted to *Physics of Fluids*, July 2013.

Zhang, C., Valentini, P., and Schwartzentruber, T.E., "A Nonequilibrium-Direction-Dependent Rotational Energy Model for use in Continuum and Stochastic Molecular Simulation", In-press, *AIAA Journal*, June 2013.

Norman, P., Valentini, P., and Schwartzentruber, T.E., "GPU-Accelerated Classical Trajectory Calculation Direct Simulation Monte Carlo Applied to Shock Waves", *J. Comp. Phys.*, 247 (2013), pp. 153-167.

Valentini, P., Tump, P. A., Zhang, C., and Schwartzentruber, T.E., "Molecular dynamics simulations of shock waves in mixtures of noble gases", *Journal of Thermophysics and Heat Transfer*, Vol. 27, No. 2 (2013), pp. 226-234.

Valentini, P., Zhang, C., and Schwartzentruber, T.E., "Molecular dynamics simulation of rotational relaxation in nitrogen: implications for rotational collision number models", *Physics of Fluids*, Vol. 24 (2012), pp. 106101-1 – 106101-23.

Full-Length Conference Papers (8):

Schwartzentruber, T.E. and Boyd, I.D. "Progress and Future Prospects for Particle-Based Simulation of Hypersonic Flow", AIAA Paper 2013-2613, June 2013, presented at the 43rd Fluid Dynamics Conference, San Diego, CA.

Nompelis, I. and Schwartzentruber, T.E., "Strategies for Parallelization of the DSMC Method", AIAA Paper 2013-1204, Jan. 2013, presented at the 51st AIAA Aerospace Sciences Meeting, Grapevine, TX.

Zhang, C. and Schwartzentruber, T.E., "A Nonequilibrium-Direction-Dependent Rotational Energy Model for use in Continuum and Stochastic Molecular Simulation", AIAA Paper 2013-1202, Jan. 2013, presented at the 51st AIAA Aerospace Sciences Meeting, Grapevine, TX.

Norman, P. and Schwartzentruber, T.E., "Classical Trajectory Calculation Direct Simulation Monte Carlo: GPU Acceleration and Three Body Collisions", AIAA Paper 2013-1200, Jan. 2013, presented at the 51st AIAA Aerospace Sciences Meeting, Grapevine, TX.

Valentini, P., Zhang, C., and Schwartzentruber, T.E., "A directional rotational relaxation model for nitrogen using molecular dynamics simulation", 28th International Symposium on Rarefied Gas Dynamics, AIP Conf. Proc. 1501, 519-526 (2012); doi: 10.1063/1.4769583

Valentini, P., Zhang, C., and Schwartzentruber, T.E., "Investigation of rotational relaxation in nitrogen via Molecular Dynamics simulation", AIAA Paper 2012-2995, June 2012, presented at the 43rd AIAA Thermophysics Conference, New Orleans, LA.

Valentini, P., Tump, P. A., Zhang, C., and Schwartzentruber, T.E., "Molecular dynamics simulations of shock waves in dilute gas mixtures", AIAA Paper 2012-225, Jan. 2012, presented at the 50th AIAA Aerospace Sciences Meeting, Nashville, TN.

Schwartzentruber, T.E., Valentini, P., Tump, P., "Molecular Simulation of Nonequilibrium Hypersonic Flows", The Proceedings of the 7th Aerothermodynamics Symposium, ESA Special Publications SP-692, Brugge, Belgium, May 2011.

II. Introduction and Existing State-of-the-Art

Currently, the two main computational tools used by the aerothermodynamics community to model hypersonic flows are: (1) Computational Fluid Dynamics (CFD) methods, which solve the multi-temperature Navier-Stokes equations with chemical reaction source terms and, (2) the direct simulation Monte Carlo (DSMC) particle method [1], which simulates the Boltzmann equation [2] and is therefore accurate for highly nonequilibrium flows relevant to rarefied flows and sharp flow features with small length scales. Currently, both CFD and DSMC use essentially the same physical models for rotational-vibrational excitation and dissociation phenomenon, which are based on a limited number of near-equilibrium experiments performed at low temperatures. The purpose of the current research is to develop a new modeling capability, based on computational chemistry, to provide a more fundamental understanding and develop more accurate thermochemical models for CFD and DSMC.

Despite operating on molecular quantities, DSMC currently employs the same empirical transport, internal energy, and chemical models used in CFD methods. For example, the models most widely employed in CFD codes include the Park model for air dissociation [3], the Millikan and White rates for vibrational relaxation [4], Blottner curve fits for viscosity [5] and Wilke's mixing rule for diffusion [6]. These rates are parameterized as being temperature dependent (typically in Arhenius or power-law form). For DSMC, these empirically constructed transport, relaxation, and reaction rates are simply converted from functions of temperature and re-written as probabilities based on relative collision energy, then subsequently applied to individual DSMC particle collisions [7-9]. Thus under continuum gas conditions, DSMC results are ensured to be consistent with CFD results (by their very construction). However, this 'top-down' (phenomenological) modeling approach is inherently limiting, since empirical rates for complex interactions are often absent (difficult to determine experimentally) or greatly extrapolated for hypersonic conditions. Furthermore, their accuracy in non-equilibrium regions is certainly questionable.

For example, discrepancies between high-speed wind-tunnel experimental measurements and numerical simulations are attributed to the uncertainty in vibrational relaxation and dissociation rates in high temperature air [10]. Very recently, discrepancy between such experiments and simulations has been attributed to possible order-of-magnitude uncertainty in oxygen recombination rates [11]. Furthermore, the lack of collision cross-section data leads to significant uncertainty in diffusive transport through high-temperature boundary layers [12], and therefore uncertainties in predicted surface heating rates. Finally, collisional non-equilibrium has been shown to be significant even at altitudes where continuum (CFD) analysis is thought to be accurate [7] and may therefore require non-equilibrium internal energy/chemistry modeling and kinetic simulation (DSMC).

The uncertainty in such rates is a major hurdle facing predictive simulation capabilities for hypersonic flows. This has prompted the development of extended vibrational models [13] and even models where each rotational and vibrational energy level is represented as its own species in computationally intensive "state-to-state" simulations. Recently, computational chemistry researchers at NASA Ames Research Center have used quantum computations to fit very detailed Potential Energy Surfaces (PES) for interactions between two and three nitrogen atoms, and are currently working on PES for four atoms [14,15]. These quantum-computed PES, corresponding to all possible inter-atomic orientations, are used to 'fit' a force-field that can be used in so-called Quasi-Classical-Trajectory (QCT) Molecular Dynamics (MD) simulations of collisions. NASA researchers have simulated millions of individual collisions using QCT-MD and compiled a database of collision cross-sections for the purpose of integration to obtain temperature-dependent rate data for use in CFD models [15]. For use in the DSMC method, Motsumoto *et al.* developed the Dynamic Molecular Collision (DMC) model [16] specifically for the translational-rotational energy transfer in diatomic nitrogen. Many isolated collisions were performed using MD with an appropriate interatomic potential and a database of collision cross-sections and pre/post energy distributions was compiled and used within the DSMC method. More recently, instead of performing isolated MD collisions, Kotov and Surzhikov [17] and Kantor *et al.* [18] simulated the dissociation of air, and oxygen-hydrogen combustion, respectively, in a periodic box using pure MD for the entire system of

molecules. However, both studies report being severely limited in the number of simulated molecules, being restricted to very high densities. The proposed research seeks to vastly improve upon such research.

The goal of the current research is to develop complete 'bottom-up' gas-phase collision models for high temperature dissociated air for use in both DSMC *and* CFD methods. A key advancement required to achieve this goal is the development of accelerated computational chemistry (molecular dynamics –MD) methods designed specifically for dilute gases. The accelerated MD methods developed by our research are capable of directly incorporating state-of-the-art interatomic potentials (that govern the interaction forces between individual atoms) from computational chemistry as the only modeling assumption. Such a capability enables new DSMC and CFD model development and a deeper understanding of energy exchange and reaction processes in hypersonic flows at the most fundamental level. In the original proposal we described ideas to develop pure MD simulations and accelerated MD simulations that enable the simulation of 1D hypersonic flow features (such as shock waves and stagnation line profiles). However, our research has progressed dramatically beyond this, and we are able to demonstrate accelerated MD simulations of 2D and even 3D flow fields where only the interactions between atoms are considered (no collision or rate models are required). The result of our research is that future advances from computational chemistry can be directly incorporated into large-scale simulations of full 3D hypersonic flow fields in strong thermochemical nonequilibrium.

III. The Molecular Gas Dynamic Simulator (MGDS) DSMC Code

My research group's core capability is large-scale stochastic molecular simulation; specifically the direct simulation Monte Carlo (DSMC) method. With partial support from this grant, we have developed a new state-of-the-art, parallel DSMC code called the Molecular Gas Dynamic Simulator (MGDS) code. The code has a number of novel features. MGDS uses an embedded three-level Cartesian flow grid with automated adaptive mesh refinement (AMR). The refinement is arbitrary (non-binary) and enables accurate and efficient simulations with little user input [19-21]. In addition, MGDS contains a robust "cut-cell" subroutine that cuts complex 3D geometry from the background Cartesian grid and exactly computes the volumes of all cut cells [22]. Combined within a DSMC solver, these two features enable molecular-level physics to be applied to real engineering problems. For example, Fig. 1 shows hypersonic flow over complex satellite geometry with sharp leading edges and Fig. 2 shows the solution and adapted flow field grid for hypersonic flow over a blunt body. It is noted that since DSMC is a particle method, *the flow field grid does not need to be aligned with sharp gradients* as required by CFD methods, which solve stiff sets of discretized partial differential equations. This enables accurate DSMC simulations to be performed for flows with sharp gradients on complex 3D geometry with very little user-time required (no gridding).
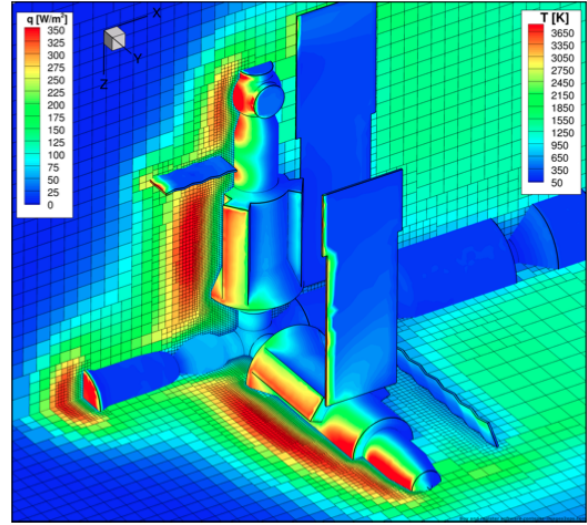

Figure 1: DSMC simulation of a satellite geometry.

In addition to the practicality for complex 3D flows, our new DSMC code acts as a bridge between computational chemistry modeling and continuum fluid mechanics. With existing parallel computer clusters, DSMC is able to perform near-continuum simulations using only molecular physics models. I believe such research has the potential to make a large impact on the field of CFD. **Upcoming sections will describe pure computational chemistry simulations and section VII will describe how the research performed under this grant has led to a new method; one which embeds computational chemistry directly into large-scale DSMC simulations, so that simulations such as those in Figs. 1 and 2 can now be performed using only atomic interaction forces as the model input.**
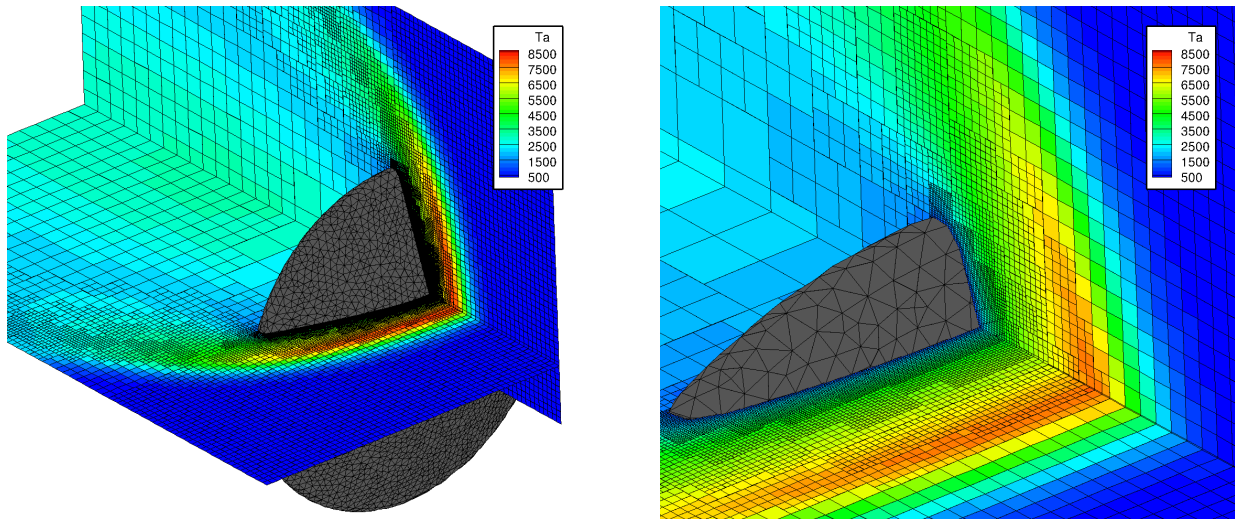

Figure 2: DSMC solution for a blunt-body flow requiring significant mesh adaptation in the fore-body and wake regions (left). Close up image of the solution and 3-level Cartesian flow field grid near the shoulder region (right).

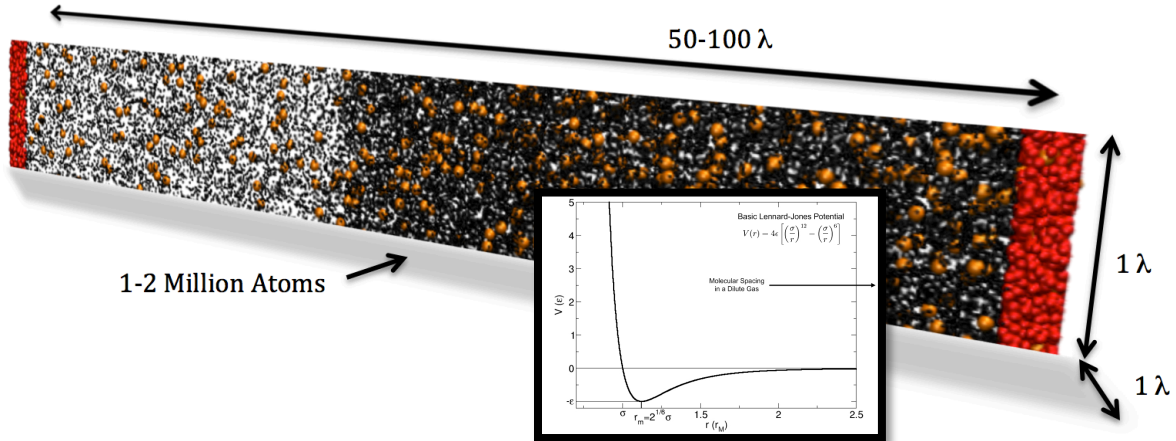## IV. All-Atom Molecular Dynamics of Shock Waves in Noble Gases

Through this grant, my research group has demonstrated that pure computational chemistry of simulation of shock waves and shock layers is computationally feasible with modest parallel computing resources. Such simulations, which are herein referred to as "all-atom molecular dynamics" (MD) simulations, require only a potential energy surface (called a "PES") that dictates the interaction forces between individual atoms, as the model input. Thus, unlike DSMC or CFD, no models for viscosity, diffusion, thermal conductivity, internal energy relaxation, chemical reactions, cross-sections, or even state-resolved probabilities/rates are required. Rather, every real atom in the system (such as the thin column containing a normal shock depicted in Fig. 3) is simulated. Each atom interacts with its neighboring atoms through a potential energy surface (PES), such as the simple Lennard-Jones (LJ) PES [23] shown in the inset of Fig. 3, which is given by the following equation:

$$\psi(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

where r_{ij} is the distance between atoms i and j, and ϵ and σ are constants specific to the species (i and j) of the interacting atoms. The motion of all atoms is then computed by integrating Newton's law of motion:

$$\dot{r}_i = v_i,$$

$$F_i(r_{ij}) = m\dot{v}_i = \sum_{j=1}^{N} \frac{d\psi(r_{ij})}{dr_{ij}} \frac{r_{ij}}{r_{ij}},$$

where N is the total number of neighboring atoms that influence atom i (usually prescribed to be within a conservative cutoff radius of atom i). Thus, such simulations are fundamental and extremely general, as the only simulation input is the PES (for example, the LJ PES shown above). The highly scalable MD code, LAMMPS [24], can be used to perform the simultaneous integration of many millions of atoms. LAMMPS is freely available from Sandia National Laboratory [25] and thus such MD simulations are repeatable by other researchers in the field.

Figure 3: Schematic of an all-atom molecular dynamics (MD) simulation of a normal shock wave. Inset shows a simple Lennard-Jones (LJ) potential energy surface (PES) dictating atomic interaction forces.

The main point of this section is to demonstrate that for gas systems where accurate PES have been well-established, such pure MD simulations of shock waves can be compared directly with experimental results. **We have carefully verified and validated our pure MD simulations with a large amount of experimental data.** Figure 4 shows results for pure argon, where the shock thickness computed by MD is in excellent agreement with experimental data from Alsmeyer and the simulations are able to precisely

resolve the bi-modal velocity distribution functions throughout the shock wave. **Complete details are fully described in our recent journal articles [26,27].**
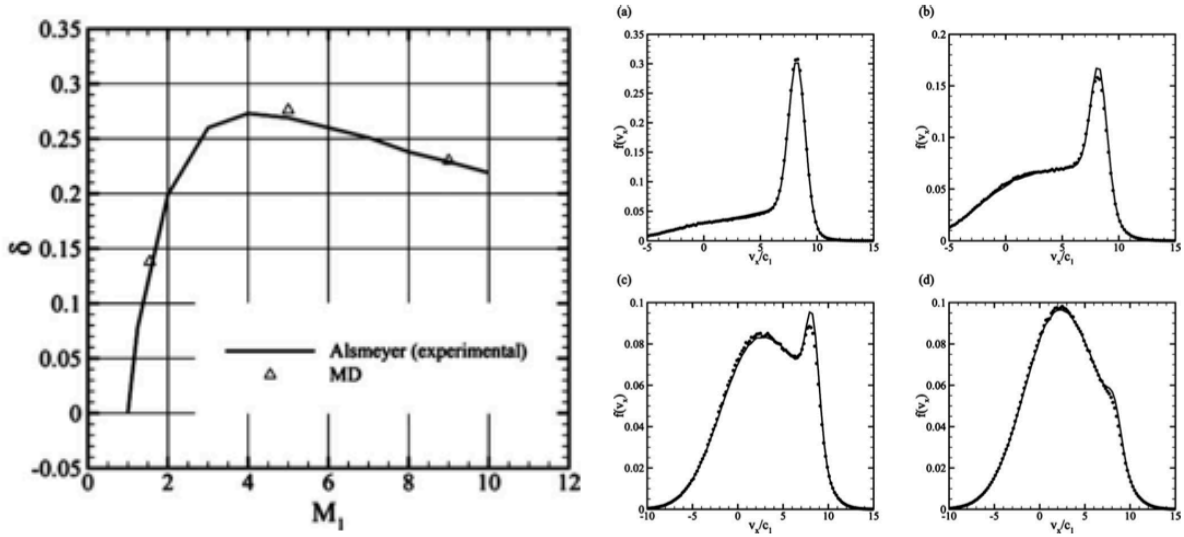
Figure 4: Pure MD simulation results for normal shock waves in argon. Shock thickness results vs. experiment (left) and velocity distribution functions within the shock (right).

We then performed pure MD simulations of mixtures of noble gases for which a great deal of experimental data exists. Results for argon-helium mixtures are shown in Figs. 5 and 6, and results of xenon-helium mixtures are shown in Fig. 7. For such flows, there is a large mass disparity between helium atoms (light) compared to argon and xenon atoms (heavy). This causes a species concentration separation within the shock wave due to diffusion effects, and the simulations are in excellent agreement with experimental results. These pure MD simulations also demonstrate that very precise results are computationally feasible even for mixtures with trace species (as low as 1.5% in some simulations). **Complete details are fully described in our recent journal article [28].**
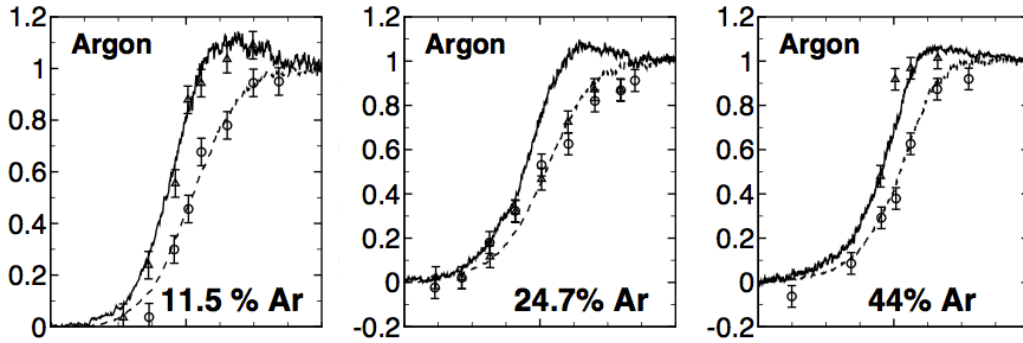
Figure 5: Argon temperature profiles within a normal shock wave in an argon-helium mixture. Symbols are experimental data (T_x: triangles, $T_y=T_z$: circles), lines are MD simulation results.
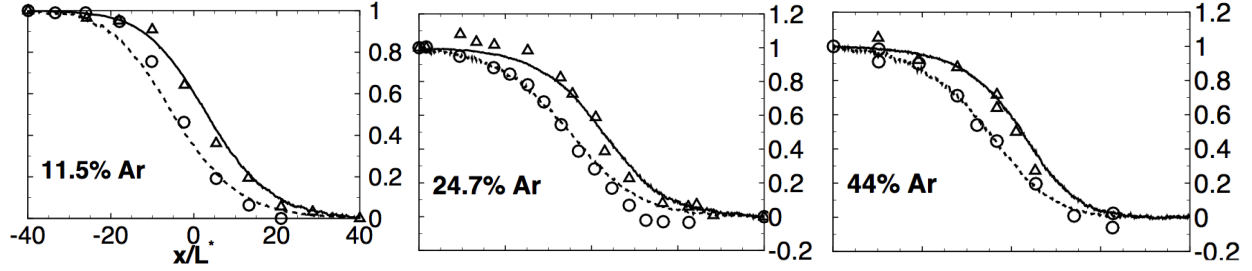
Figure 6: Species velocity profiles within a normal shock wave in an argon-helium mixture. Symbols are experimental data (Argon : triangles, Helium : circles), lines are MD simulation results.
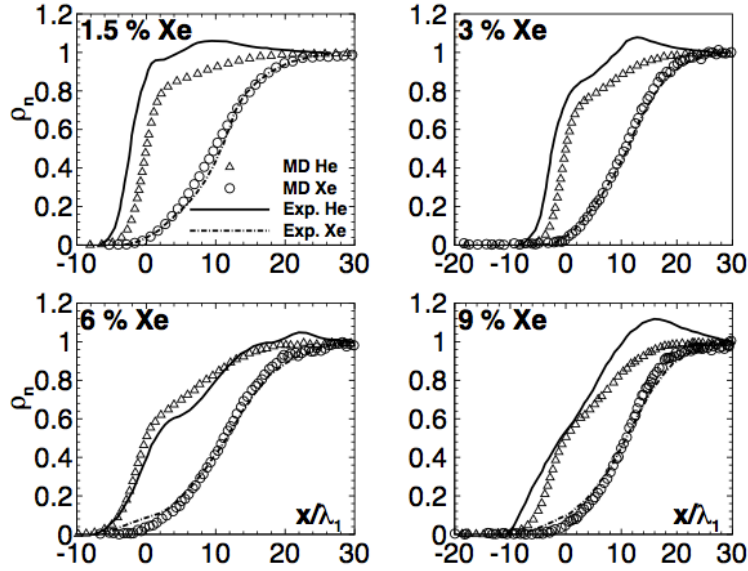

Figure 7: Species temperature profiles within a normal shock wave in an xenon-helium mixture. Symbols are experimental data (Helium: triangles, Xenon : circles), lines are MD simulation results.

V. All-Atom Molecular Dynamics of Shock Waves in Nitrogen (Rotational Relaxation)

After carefully validating our MD simulations for monatomic gas mixtures, we moved on to diatomic gases where rotational excitation of the molecules was now an important physical aspect. We performed simulations of shock waves in nitrogen, using a site-to-site LJ potential, that is accurate for nitrogen at relatively low temperatures (<3000 K) where vibrational excitation can be safely ignored. **We first validate the PES by computing the viscosity of nitrogen over a wide temperature range and comparing with experimental data. Validating the viscosity (essentially the collision rate) predicted by a PES is a crucial step that should always be performed first.** More advanced physics, such as rotational and vibrational relaxation, and chemical reactions are always defined relative to the collision rate. For example, "collision numbers" (Z_{rot}, Z_{vib}) and reaction probabilities are used as models that determine what fraction of collisions results in internal energy exchange and reactions. Thus, if the collision rate (i.e. the viscosity) is not modeled correctly, then the interpreted rates of internal energy transfer and chemical reactions will be incorrect as well. We determine the viscosity predicted by a PES using the Green-Kubo theory [29,30], i.e., by computing the autocorrelation function of the off-diagonal pressure tensor terms, which were estimated using the virial equation. After validating the viscosity prediction, we performed normal shock calculations and compared the results to experimental data from Robben and Talbot. Figure 8 shows MD results compared to experiment for the density and rotational temperature profiles in Mach 7 and 12.7 nitrogen shock waves. The experimental data set also included

rotational energy distribution functions throughout the shock. These are plotted in in Fig. 8, compared to MD simulation results. The distributions are seen to start at a Boltzmann Distribution (BD) corresponding to the upstream temperature and relaxing to a BD corresponding to the downstream temperature. However, within the shock wave, the rotational energy distributions are seen to be non-Boltzmann. **Complete details are fully described in our recent journal article [31].**
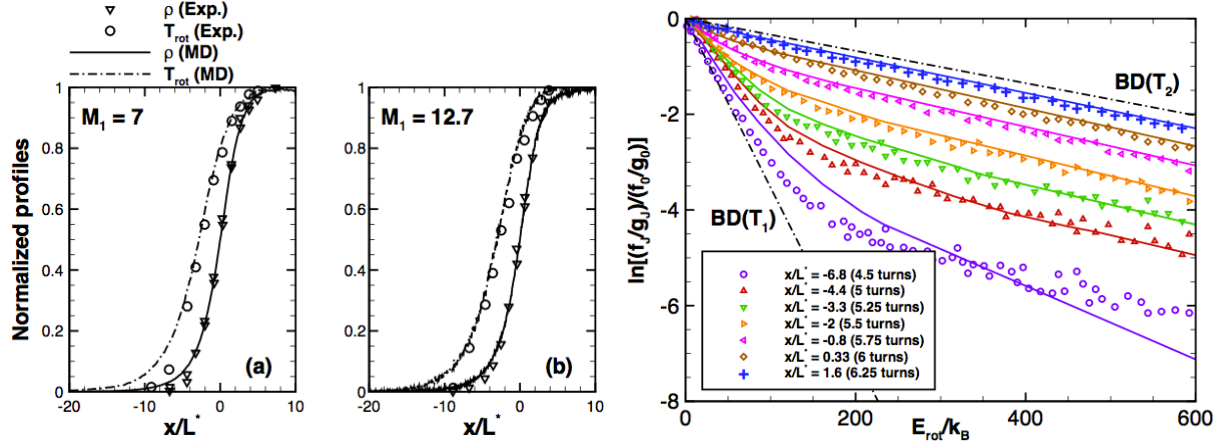

Figure 8: MD simulation results compared to experiment for nitrogen shock waves. Density and rotational temperature profiles within the shock waves (left). Rotational energy distribution functions (right).

After validating our nitrogen simulations with experimental data, we were able to analyze the large amount of data produced by such pure MD simulations to solve a long-standing problem regarding translational-rotational energy transfer. Specifically, it had been postulated in the literature that the rate of rotational-translation energy transfer in a gas may not be a function of the equilibrium temperature only (the approach taken by all existing models), but instead, may depend strongly on the initial degree of nonequilibrium and the direction towards the equilibrium state (i.e. compressing vs. expanding flows). In a 1998 review article on this topic [32], Wysong and Wadsworth concluded that, "*the primary complicating factor, and that which may be of most use in improving phenomenological models of the process, is the potentially large effect of the size and sign of the initial deviation from equilibrium*". In addition to normal shocks, we performed isothermal relaxation calculations with

Figure 9: Rotaional temperature profiles for isothermal relaxation MD simulations for different initial conditions.

pure MD where molecules were initialized (in a periodic box – zero-dimensional) with their rotational energies out of equilibrium with translation and they relaxed via collisions to the equilibrium state. As seen in Fig. 9, we observed that, for the same equilibrium temperature, the rate of rotational energy relaxation varied significantly depending on the initial state. Specifically, our MD simulations clearly showed that rotational relaxation rates were a strong function of both the direction to equilibrium and the initial degree (magnitude) of nonequilibrium. Figure 10 shows how, for the same equilibrium temperature (T_{inf}), compressing flows ($T_{tr}^0 - T_{rot}^0 > 0$) have short relaxation times (τ_{rot}), while for expanding flows ($T_{tr}^0 - T_{rot}^0 < 0$) relaxation times are much larger.
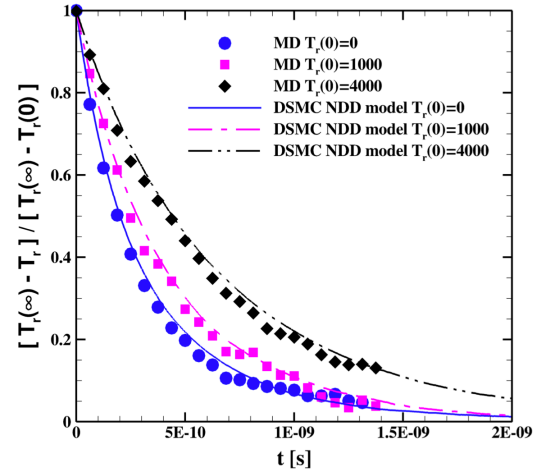
Currently, the most widely used rotation model is the Parker model, which only models rotational relaxation (τ_{rot} or equivalently Z_{rot}) in function of the equilibrium temperature. Therefore, the Parker

model only accounts for a line ($T_{tr}^0 - T_{rot}^0 = 0$) extracted from our data in Fig. 10. The Parker model along with our data extracted on this line are shown in Fig. 11 along with other equilibrium results from computational chemistry. Also plotted in Fig. 11 is the available experimental data that is seen to have a huge variation, and was only interpreted/parameterized in terms of the equilibrium temperature. Our results, shown fully in Fig. 10, are much more general and conclude that the magnitude of initial nonequilibrium and direction to the equilibrium state have a much stronger effect on rotational relaxation that the equilibrium temperature. Enabled by our MD simulation capability, we were the first to quantify these effects for nitrogen. Our most recent paper, in the AIAA Journal [33], presents a new "direction-dependent" rotation model (the NDD model) for use in both DSMC *and* CFD. In addition to the new model, this article makes a number of further contributions including a mathematical formulation that ensures detailed balance for DSMC models, and a mathematical framework that rigorously integrates a DSMC model (in the limit of equilibrium) to obtain a consistent model for CFD. The new DSMC model parameterizes the probability of rotational energy exchange as a function of both the rotational energy and translational energy involved in a collision:
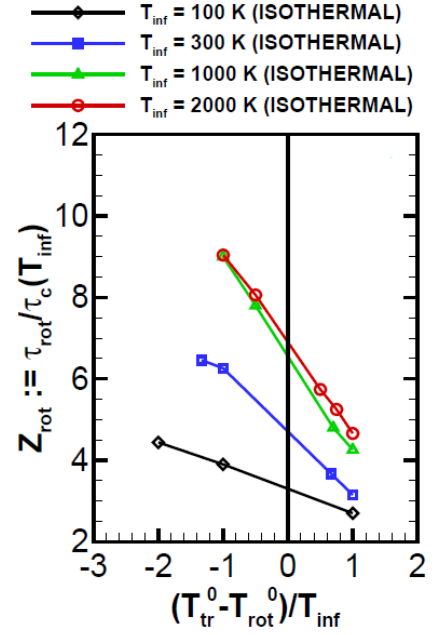

Figure 10: Rotational relaxation rates predicted by MD simulation in function of both T_{tr} *and* T_{rot}.

$$p_{rot}^{NDD}(\varepsilon_t, \varepsilon_r) = min\{C_n C_a \; \tilde{p}_{rot}(\varepsilon_t, \varepsilon_r), \frac{1}{2}\}$$

$$\tilde{p}_{rot}(\varepsilon_t, \varepsilon_r) = \frac{\Gamma(\frac{\zeta_t}{2})\Gamma(\frac{\zeta_r}{2})}{\Gamma(\frac{\zeta_t}{2}+n)\Gamma(\frac{\zeta_r}{2}-n)Z_r^\infty} \left[1 + (\frac{\zeta_t}{2}+n-1)\frac{k_B T^*}{\varepsilon_t}\right] \left(\frac{\varepsilon_t}{\varepsilon_r}\right)^n$$
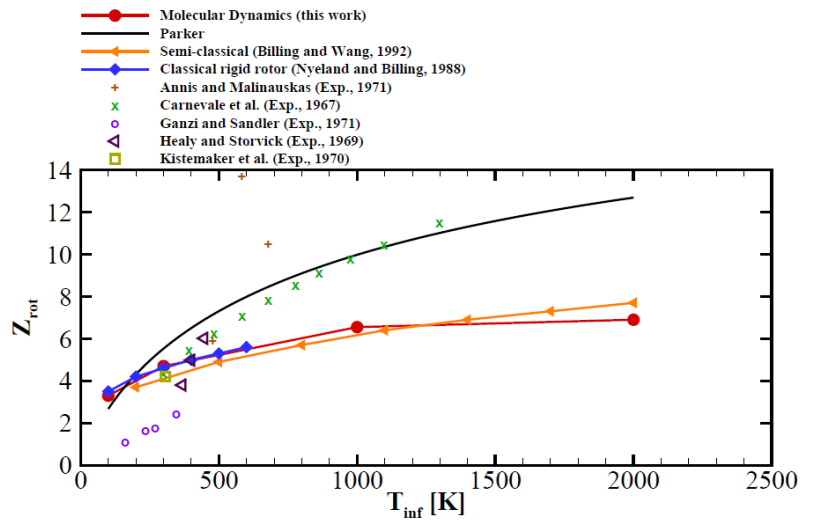
When integrated in the limit of equilibrium (Maxwell-Boltzmann translational and rotational energy distribution functions), the following temperature dependent model results, which is suitable for use in multi-temperature Navier-Stokes (CFD) simulations:

$$Z_{rot}(T_t, T_r) = \frac{Z_r^\infty}{1 + \frac{T^*}{T_t}} \left(\frac{T_r}{T_t}\right)^n$$

Finally, this new NDD model was used to compute full shock wave profiles and compare to pure MD solutions. We found that the new NDD model, which correctly models the direction-dependence of the relaxation rate, is able to accurately reproduce full MD results while the existing Parker model is not (Fig. 12). Furthermore, the NDD model was also able to successfully predict rotational relaxation in expanding flows, while the Parker model was not. Thus this research, used novel pure MD simulations to discover new
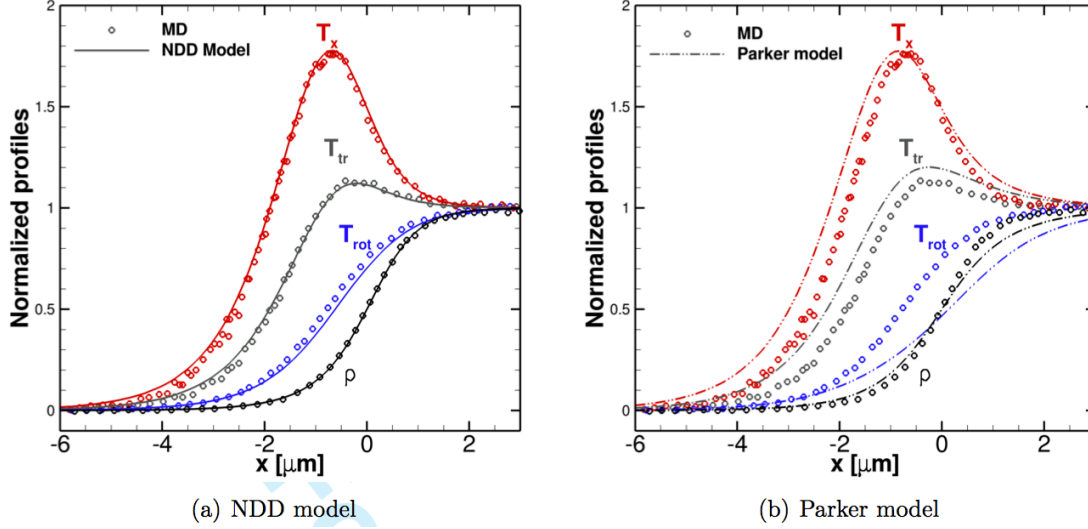

Figure 11: Rotational relaxation rate in the limit of thermal equilibrium ($T_{tr}=T_{rot}$) from various sources.

physical processes import in rotational relaxation. These high fidelity calculations provided the data needed to create new DSMC and CFD models. **Complete details are fully described in our recent journal articles [31,33].**

(a) NDD model   (b) Parker model

Figure 12: Normal shock calculations using DSMC with the new NDD model (a) and the Parker model (b) compared with a solution from pure MD simulation.

## VI. All-Atom Molecular Dynamics of Shock Waves in Nitrogen (Rotational-Vibrational Excitation)

After studying translational-rotational energy exchange, we moved on to study translational-rotational-vibrational energy exchange and dissociation. The temperature range considered is now much higher and it is known that vibrational processes are sensitive to the "repulsive wall" region of the PES (very close range atomic interactions). In this energy range, we use a potential energy surface (PES) from Ling and Rigby (LR) [34] that has been used by a number of researchers to study rotation and vibration in nitrogen at high temperatures [35,36]. The LR PES that governs the interaction between an atom and atoms of neighboring molecules (the *inter*molecular potential) is given by:

$$\phi(r_{ij}) = D\exp(-\alpha r_{ij} - \beta r_{ij}^2) - f_d(r_{ij})\frac{C_6}{r_{ij}^6}$$

$$f_d(r_{ij}) = \exp\left(-\frac{1}{4}\left[\left(\frac{\delta}{r_{ij}}\right)^2 - 1\right]\right)$$

and is parameterized for diatomic nitrogen [34]. The interactions between atoms of the same molecule (the *intra*molecular potential) is described by the Harmonic Oscillator potential (HO), parameterized for nitrogen. This means that for simulations using the LR + HO potentials that molecules cannot dissociate and only rotational-vibrational processes are simulated. In later simulations we use increasing degrees of anharmonicity and finally a Morse-type potential (anharmonic oscillator - AHO), which allows for molecular bond breaking and dissociation. **It is important to note that simulations performed with any of these PES operate on individual atoms only (position and velocity of atoms). Thus there is no assumed decoupling of rotational and vibrational energies within a simulation.** Only as a post-processing step do we analyze the positions and velocities of atoms bonded in nitrogen molecules to compute rotation and vibrational energies. **This is a unique aspect of such MD simulations and enables us to study ro-vibrational coupling effects where no other numerical method can.**

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We performed a large number of isothermal relaxation calculations, similar to those performed for Fig. 9, except now at much higher temperatures, where significant vibrational energy exchange occurs. Two sample results are shown in Fig. 13, and the results are very interesting.
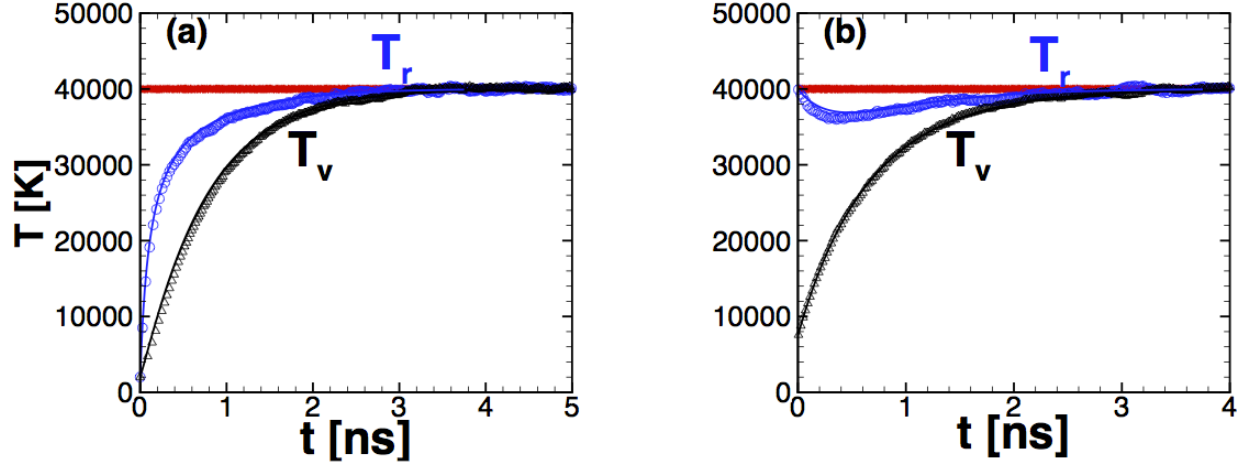
Figure 13: Isothermal relaxation simulations using pure MD with rotating and vibrating nitrogen. Symbols are MD solutions and lines are solutions to the *modified* Jeans and Landau-Teller equations that we propose.

In Fig. 13 (a), initially $T_{rot} = T_{vib} \ll T_t$ and as the MD simulation proceeds the rotational energy increases first, followed by the vibrational temperature. In Fig. 13 (b), initially $T_{vib} \ll T_{rot} = T_t$ and as the simulation proceeds the vibrational energy increases, however, the rotational energy actually decreases first, before increasing back into equilibrium with translation. Both of these initial conditions are representative of the gas state immediately downstream of a strong shock wave. We find that no existing rotational or vibrational energy transfer models are capable of matching these trends.

At the continuum level, the equation typically used to describe the relaxation process is of the form:

$$\frac{d\varepsilon_i}{dt} = \frac{\varepsilon_i^*(T_t) - \varepsilon_i(t)}{\tau_i}, \tag{1}$$

where $\varepsilon_i^*(T_t) = \zeta_i/2\, k_B T_t(t)$ represents the instantaneous equilibrium energy associated with the i-th internal energy mode with ζ_i degrees of freedom and k_B is Boltzmann's constant. $T_t(t)$ is the time-dependent translational temperature of the system. For rotation (vibration), Eq. 2 is referred to as the Jeans (Landau-Teller) equation. It is common to express

$$\tau_i = Z_i \tau_c, \tag{2}$$

where τ_i is the mean collision time (a function of T_t) and Z_i is a so-called relaxation collision number.

For an isothermal relaxation, where the translational temperature (T_t) remains a constant, the solution to equation (1) for the rotational temperature profile is:

$$\Delta T_{rot}^{iso}(t) = \Delta T_{rot}^0 \exp(-t/\tau_{rot}) = \Delta T_{rot}^0 \exp(-t\nu_c/Z_{rot})$$

For lower temperatures we found that all MD rotational relaxation solutions were well-fit by such an expression (for example see the curves in Fig. 9 and the Z_{rot} values in Fig. 10). However, the solution for T_{rot} in Fig. 13 (a) cannot be fit by such an expression. Likewise, since equation (1) relaxes either rotational (or vibrational) energy into equilibrium with only translational energy (which is fixed for the simulations in Fig.. 13), the decrease in rotational temperature seen in Fig. 13 (b) cannot be predicted by equation (1). What is happening at these high temperatures is that there is energy exchange directly between rotational and vibrational energy modes during collisions of nitrogen molecules. We find that an additional term is required in Eq. (1) in order to account for this physical process. Specifically:

$$\frac{d(\frac{1}{2}\zeta_r T_r)}{dt} = \frac{\frac{1}{2}\zeta_r T_t(t) - \frac{1}{2}\zeta_r T_r(t)}{\tau_r} + \Omega \qquad \frac{d(\frac{1}{2}\zeta_v T_v)}{dt} = \frac{\frac{1}{2}\zeta_v T_t(t) - \frac{1}{2}\zeta_v T_v(t)}{\tau_v} - \Omega$$

$$\Omega = \frac{\frac{1}{2}(\zeta_r + \zeta_v)T_v(t) - \frac{1}{2}(\zeta_r + \zeta_v)T_r(t)}{\tau_{rv}}$$

That is, **in order to match the relaxation behavior seen in our MD calculations one must consider not only τ_v and τ_r (relaxation defined in reference to translational energy), but also a coupled relaxation parameter, τ_{rv}.** We were then able to determine each of the parameters τ_v, τ_r, and τ_{rv} for nitrogen from our MD simulations; the results are shown in Fig. 14. In order to interpret all parameters from our MD simulations we had to first determine the viscosity ($\sim\tau_c$) of the LR + HO PES over the entire temperature range, followed by determining the direction-dependent rotational relaxation behavior of this potential (τ_{rot} - very similar to that presented in Fig. 10, but over a much larger temperature range), followed by a validation of the predicted vibrational relaxation at low temperatures compared to the experimental data of Millikan and White. This, then allowed us to determine the τ_{rv} required to account for the rotational energy coupling to vibration (as seen in Fig. 13 (b)), and finally enabled us to determine the resulting τ_{vib} to match all MD profiles.

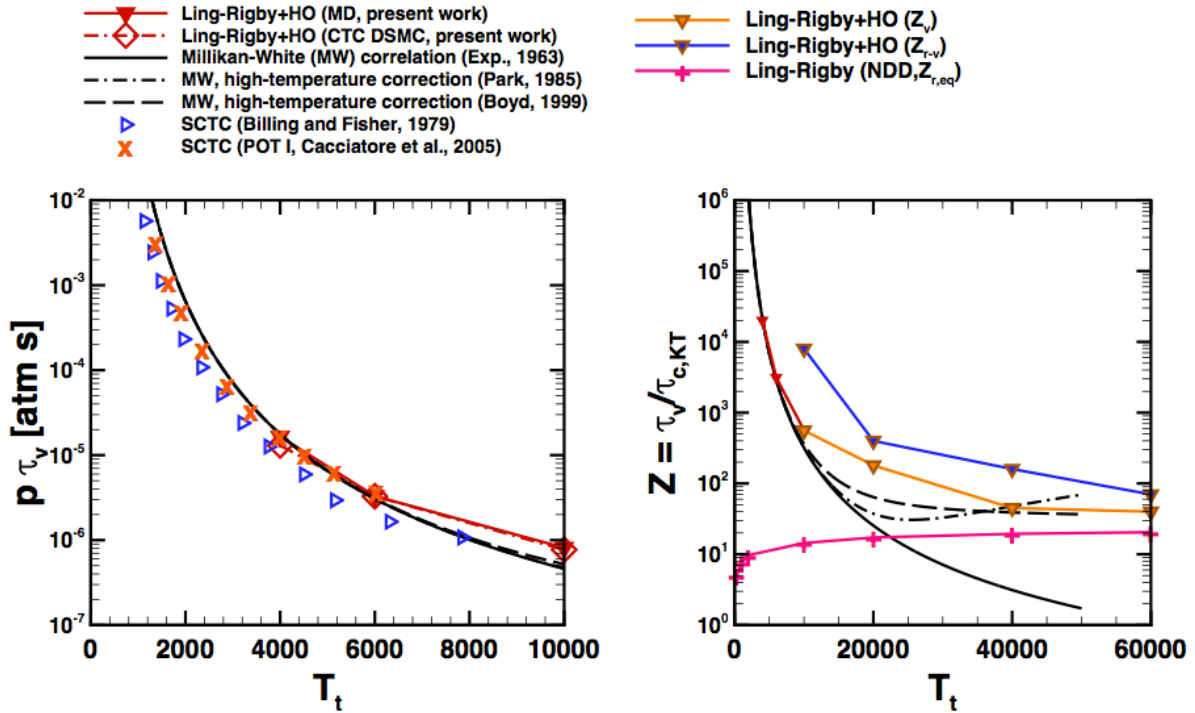**Figure 14:** Relaxation time constants and collision numbers (τ_r – Z_r, τ_v – Z_v, and τ_{rv} – Z_{rv}) determined by pure MD simulations in function of equilibrium (translational) temperature.

We report two major findings. First, rotational and vibrational relaxation times (Z_{vib} and Z_{rot}) approach each other at high temperatures (Fig. 14 – right), and thus both processes are equally important. Whereas, existing CFD models account only for vibrational relaxation and assume that rotational energy is in equilibrium with translational energy. Second, in order to match the relaxation behavior seen in our MD calculations one must consider not only τ_v and τ_r (relaxation defined in reference to translational energy), but also a coupled relaxation parameter, τ_{rv}. The magnitude of the new term (which includes τ_{rv}), is such that it only becomes significant at high temperatures, while at low temperatures, the original Jeans and Landau-Teller equations are recovered. The additional term represents relaxation of rotational and vibrational energy modes to an equilibrium *internal* energy in addition to the original equations, which represent relaxation to an equilibrium *translational* energy. Our proposed modification alters the energy transfer between energy modes at high temperatures where these processes are coupled to dissociation. Complete details are fully described in a journal article we have just submitted for publication and that is currently under review [37].

Although the temperatures in Figs. 13 and 14 are well above the equilibrium dissociation temperature for N_2, we note that in a nonequilibrium shock layer there will be substantial molecular collisions within this range of translational energies before the gas-molecules are fully dissociated. Furthermore, although not shown in this report, our preliminary results show that increasing the anharmonicity of the PES (more realistic of actual N_2 molecules that dissociate) shifts the rotational-vibration coupling effects to lower temperatures. **Figure 15 shows a preliminary pure MD simulation of a nitrogen shock wave including dissociation. This simulation includes trans-rot-vib energy transfer with ro-vibrational coupling and dissociation.** We note that the scatter is due to the absence of atomic species in the upstream portion and the absence of diatomics the downstream portion.
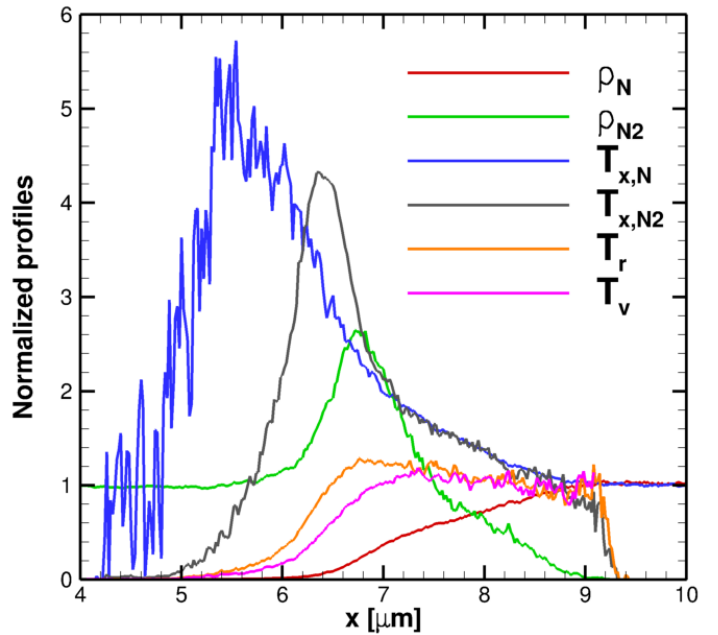

Figure 15: Preliminary pure MD simulation of a nitrogen shock wave including dissociation.

It is not yet clear to what degree such rotational-vibrational coupling ultimately affects dissociation. However, the unique modeling capabilities and expertise we have developed due to this AFOSR grant enable my research group to unravel these physical processes and understand high speed flows at the most fundamental level. We are working to confirm and refine these findings using new state-of-the-art PES that have recently been constructed as part of a large Multi-University Research Initiative (MURI) centered in the Aerospace Engineering & Mechanics and Chemistry departments at Minnesota. If we can confirm our findings and quantify the affect on dissociation chemistry, this would be a very significant contribution to the high-speed flow community.

VII. Embedding MD trajectories within DSMC Simulations

Finally, it is possible to imbed molecular dynamics trajectories directly into DSMC simulations. In this manner, the rigorous simplifications employed by DSMC are maintained; using simulator particles that each represent a large number of identical real molecules, moving simulator particles with timesteps on

the order of τ_c, and stochastically selecting collision pairs and initial orientations within volumes (computational cells) on the order of λ. However, the collision models in DSMC are completely replaced by trajectory calculations performed on arbitrary PES. This technique was introduced by Koura in 2001 as Classical-Trajectory-Calculation (CTC) DSMC [38-40] where trajectories were combined with the null-collision DSMC algorithm. As part of the current grant, we published a CTC-DSMC implementation that uses the No-Time-Counter (NTC) scheme (the most popular DSMC scheme) with a cross-section that is determined by the PES and is consistently applied as the maximum impact parameter for the trajectory calculations [41]. Since both DSMC-CTC and pure MD simulations can use the same PES as the only model input, the two particle simulation techniques can now be directly compared. For example, Fig. 16 compares CTC-DSMC and pure MD solutions for a Mach 7 diatomic nitrogen shock where a comparison between normalized density and temperature profiles is shown. The results of CTC-DSMC and MD simulations are in perfect agreement. The rotational energy distribution functions at different values of the normalized T_{rot} within the shock are also found to be exactly equivalent. The MD density and rotational temperature profiles and rotational distribution functions have been previously validated with experimental data [31]. It is noted that no DSMC collision model exists that is able to exactly reproduce the MD results to this level of precision [31,33]. Thus for the flows considered (and potentially for more complex flows), CTC-DSMC is shown to be purely a numerical acceleration technique for the MD simulation of dilute gases, since both methods require only the PES as a model input. **Complete details are fully described in our recent journal article [41].**

Although much more efficient than pure MD simulation (simulating every real atom with femtosecond timescales), CTC-DSMC remains roughly 2 to 3 orders of magnitude more computationally expensive than standard DSMC, depending on the complexity of the PES used for the trajectories. However, we have shown that CTC-DSMC calculations scale extremely well on parallel architectures (including GPU architectures [41]). Essentially, the CTC-DSMC technique automates the generation of state-to-state transition rate data. Instead of performing billions of independent trajectories to determine state-transition probabilities, the billions of trajectories are imbedded within an actual flow simulation. In this manner, the trajectories performed within a CTC-DSMC simulation are naturally those that are most relevant to the problem being simulated. The influence of specific PES can immediately be determined and variations in PES (which model the same species interactions to different accuracy) can be directly compared for full flow fields without the need to generate and converge full state-to-state cross-section models and implement in a DSMC code for each variation of a PES. Thus, CTC-DSMC may be useful in guiding the development of state-to-state models and lead to insight into physical-based model reduction strategies.
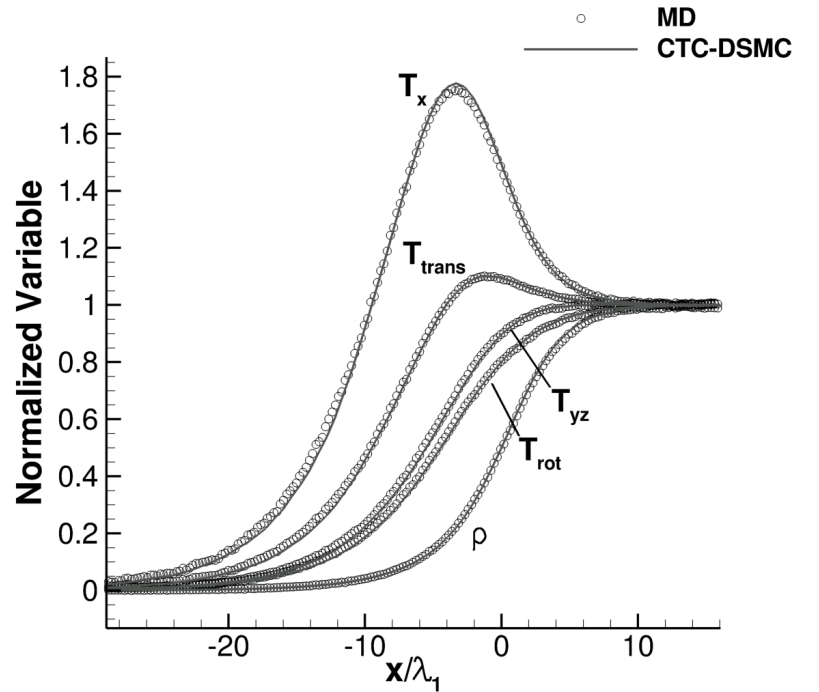
Figure 16: Comparison between CTC-DSMC and pure MD solutions for a shock wave in diatomic nitrogen.

Finally, we have demonstrated that CTC-DSMC capability allows solutions to full 3D nonequilibrium flow fields over complex geometry, with accuracy that is expected to be equivalent to full MD simulation. An example 3D solution is shown in Fig. 17 below for hypersonic flow of argon over a capsule geometry. Although this is only argon gas, the important fact is that this shock-layer solution was obtained with only a single PES as input to the simulation, and no other model. Future work will continue to develop this capability and incorporate state-of-the-art PES. While such simulations are not expected to overlap with the 3D near-continuum flows in the near future, they certainly overlap with rarefied DSMC simulations and for 2D/axi-symmetric flows, may overlap with CFD solutions if thousands of processors are used (which is feasible even now).
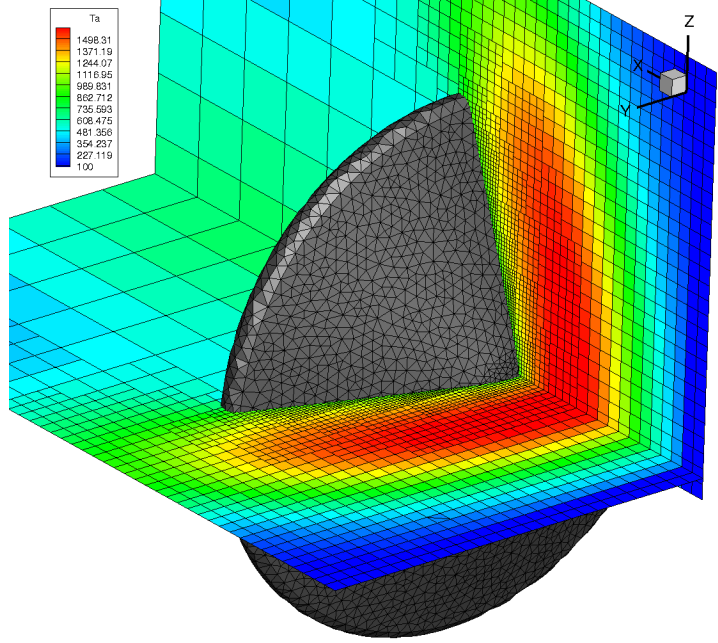
Figure 17: Three-dimensional DSMC-CTC solution for hypersonic flow of argon over a capsule geometry. This simulation required only 128 cores for 12 hours using the MGDS code.

VIII. Conclusions

1. All-atom computational chemistry (molecular dynamics – MD) simulation of normal shock waves is possible. A simulation methodology was developed and rigorously validated with experimental data for shock structure in mixtures of nobles gases and diatomic nitrogen. Precise MD simulations, able to resolve distribution functions and also species with low concentrations, are possible with moderate computational resources (100 core processors for a few days).

2. All-atom MD simulations of nitrogen discovered clear "direction-dependence" of translational-rotational energy transfer that is not captured by existing models. We found that compressing flows involve fast rotational excitation, whereas expanding flows involve slower relaxation, for the same equilibrium temperature. We developed a new model for both DSMC and CFD that reproduces experimental data and is consistent between MD, DSMC, and CFD.

3. All-atom MD simulations of nitrogen discovered rotation-vibration coupling at high temperatures. It was found that the widely used Jeans and Landau-Teller equations for rotation and vibrational energy transfer (in the multi-temperature Navier-Stokes equations) are unable to reproduce the ro-vibrational coupling found in MD simulations. We propose that an additional relaxation time ($\tau_{rot\text{-}vib}$) is required to model direct energy transfer between rotation and vibration at high temperatures and present a new ro-vibrational model. Preliminary simulations of dissociating nitrogen are also demonstrated and future work will use new, state-of-the-art, PES being developed for air species interactions at NASA Ames Research Center and also through a large AFOSR MURI grant centered at the University of Minnesota.

4. We developed a combined MD-DSMC technique that replaces the collision model in DSMC with MD trajectories and verified the method to reproduce exactly pure MD results. This is a significant advancement that enables simulation of axisymmetric and even 3D flows where a potential energy surface is the only model input. Thus, the accuracy of pure MD is maintained for full flow fields; directly linking computational chemistry with aerothermodynamics.

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5. In general, this grant has developed expertise in computational chemistry techniques themselves, their validation, their application to high temperature flows of interest, and how to use their predictions to form reduced order models for DSMC and CFD. Future work can combine all of these developments with new state-of-the-art PES being developed by computational chemists with the goal of developing new models that are consistent across all scales (MD – DSMC – CFD – Experiment). Such research would enable an understanding of hypersonic flows at the most fundamental level.

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